Synthesis of Ce substituted MFI type zeolites by mechanochemical reaction

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Abstract: Zeolites partly substituted for Al by other metals are expected to use as catalysts with high activity. In particular, we focused on Ce substituted MFI zeolite (Ce-MFI) to the application to a catalyst for the methane conversion to higher hydrocarbons. However, few papers reported Ce substituted zeolite. In this study, we have prepared Ce substituted MFI zeolite and research whether possible to incorporate into the zeolite framework. In conclusion, Ce was successfully introduced by cation addition. The result which some parts of Ce are Ce^{3+} in the zeolite framework and others are Ce^{4+} is suggested.

Keywords: Zeolite, Methane conversion, Cerium

1. Introduction

MFI zeolites partly substituted for Al by a variety of other metals are expected to use as catalysts with high activity, because, introduced metal atoms can endow MFI structure so as to influence properties, such as acidity, electron transfer, etc.. In particular, Ce substituted MFI zeolite (Ce-MFI) has attracted our attention to the application to a catalyst for the methane conversion to higher hydrocarbons. However, few papers reported Ce substituted zeolite. In this study, we have prepared Ce substituted MFI zeolite and research whether possible to incorporate into the zeolite framework.

2. Experimental

Ce-MFI was synthesized as follows. Figure 1 shows the Ball mill vessel and planetary ball mill. $Ce(OH)_4$ and Aerosil were put in the ball mill vessels. Then, they rotated at 600 rpm for 16 minutes and stood for 15 minutes. These operations repeated 96 times to mill for 24 hours in total. After milling, mechanochemical precursor was gotten as powder. Then, an aqueous solution of KCl, tetrapropylammonium hydroxide, H_2O, Carplex and mechanochemical precursor was added to a Teflon vessel. The mixture was stirred at room temperature for 48 hours. The composition of the aqueous solution was adjusted to SiO_2 : CeO_2 : KCl : TPAOH : H_2O = 1 : 0.02 : 0-0.3 : 0.4 : 30. The prepared aqueous solution was treated at 160 ˚C in an autoclave for 120 hours. Then, the samples were washed, dried at 60 ˚C and calcined at 540 ˚C for 12 hours to get Ce introduced MFI type zeolite.

Figure 1. Ball mill vessel and planetary ball mill

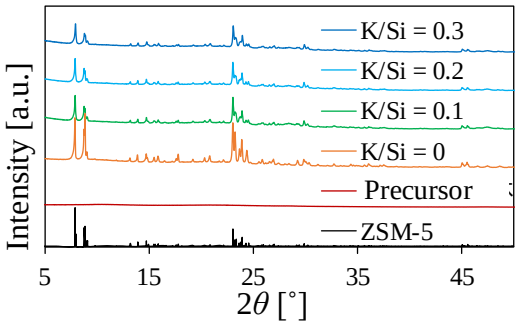

Figure 2. XRD pattern of Ce-MFI with the different K/Si ratios

Preparation ratio of K/Si	K/Si = 0	K/Si = 0.1	K/Si = 0.2	K/Si = 0.3
Ce/Si (ICP)	0.003	0.048	0.049	0.045

Table 1. ICP result of Ce-MFI with the different K/Si ratios

3. Results and discussion

Figure 2 shows the XRD pattern of Ce-MFI with the different K/Si ratios. According to this figure, other than K/Si = 0, almost the same crystallinity regardless of K^+ amount. Also, Precursor is confirmed to be amorphous. Because of this, Ce-MFI was synthesized from mechano-chemical precursor and all samples had MFI structure.

Table 1 shows the ICP results of Ce-MFI with the different K/Si ratios. This table indicates the existence of Ce atoms in the zeolite and increase of Ce introduction by K^+ addition. Thus, Ce was successfully introduced in MFI type zeolite by cation.

Figure 3 shows the SEM image of Ce-MFI with the different K/Si ratios. From particle size of K/Si = 0.2 and 0.3, reduction in particle size due to excess cation addition is confirmed.

Figure 4 shows the IR spectra of Ce-MFI with the different K/Si ratios. The valley around 1200-1000 cm^{-1} which shows the T-O-T asymmetric stretch vibration was observed. Broadened this vibration suggests the hetero atom in the zeolite framework[1,2]. Thus, Ce was introduced into the framework of MFI.

Figure 5 shows the XPS result of Ce-MFI with the different K/Si ratios. According to this figure, only Ce^{4+} peak is confirmed in K/Si = 0. On the other hand, Ce^{3+} and Ce^{4+} peaks are confirmed in K/Si = 0.1-0.3. These results indicate the introduction of Ce^{3+} and Ce^{4+} in the zeolite framework

4. Conclusions

In conclusion, Ce was successfully introduced by cation addition. The result which some parts of Ce are Ce^{3+} in the zeolite framework and others are Ce^{4+} is suggested. Next, we aim to the divided introduction of Ce^{3+} and Ce^{4+}, and evaluate of their catalytic activity.

References

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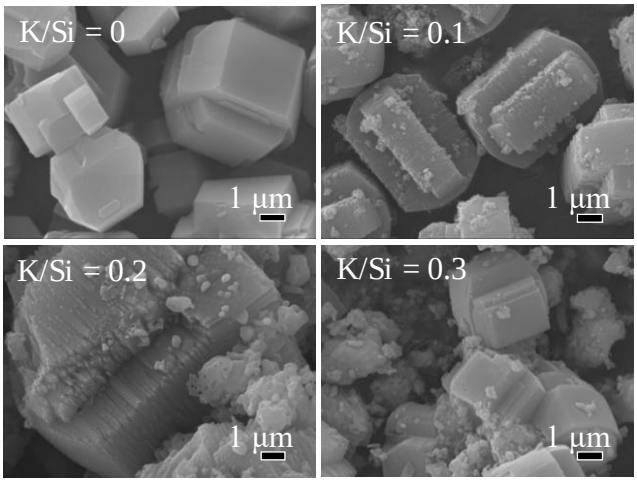

Figure 3. SEM image of Ce-MFI with the different K/Si ratios

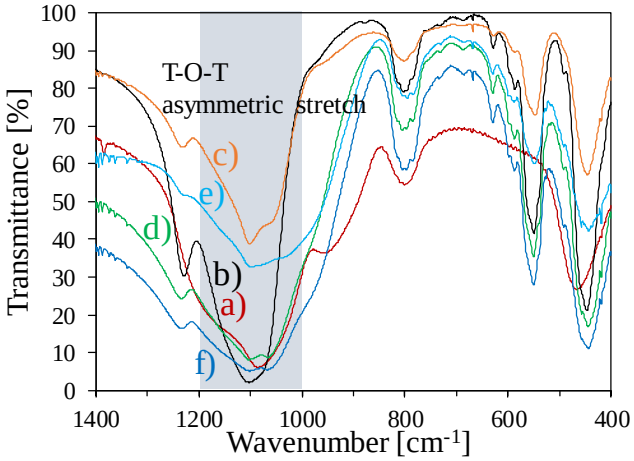

Figure 4. IR spectra of Ce-MFI with the different K/Si ratios
a) Mechanochemical precursor, b) Silicalite-1,
c) K/Si = 0, d) K/Si = 0.1, e) K/Si = 0.2, f) K/Si = 0.3

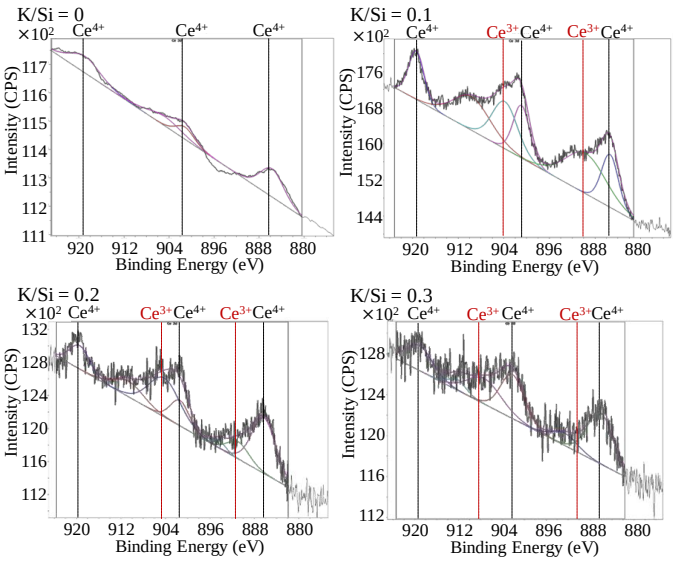

Figure 5. XRD pattern of Ce-MFI with the different K/Si ratios